

The Scientific Basis for Plutonium Stabilization With Particular Emphasis on Gas Generation

Thermodynamics, Kinetics, Radiolysis and
Modeling Efforts Directed toward Predicting
and Understanding Gas Generation in
Specific Actinide Oxide Storage Conditions

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Scope - Core Technology Project

Interactions of water and various other small molecules with plutonium and uranium metals and their oxides are being studied from many scientific viewpoints. Heterogeneous kinetics experiments consisting of pressure-volume-temperature (PVT) measurements complemented with modern surface science techniques are being employed. Fundamental details of radiolytic gas generation are also being addressed from the standpoint of adsorbed moisture. Deliverables include thermodynamic and kinetic values pertinent to understanding the long-term storage of actinide and actinide oxide materials. These values are derived and evaluated for use in gas generation modeling schemes of importance in assessing and validating the proposed revisions to the 3013 storage standards. This work will elucidate the science underlying the thermal stabilization and long-term stable storage of nuclear materials.

The Scientific Basis for Plutonium Stabilization With Particular Emphasis on Gas Generation

Essential Questions Addressed By this Work:

Can we safely predict and account for all behaviors in the storage of actinide oxide materials?

Definition of the Problem in Terms of the 3013 Standard

Problems and Opportunities:

- Understanding the physical, chemical, and radiolytic mechanisms for gas generation in typical and atypical material types and processing conditions
- Identification of data needs for successful modeling
- Identification and experimental re-determination of results that present conflicting conclusions
- Complimentary techniques and approaches needed to confirm results and provide data for modeling efforts

The Scientific Basis for Plutonium Stabilization With Particular Emphasis on Gas Generation:

Project Components:

- ❖ **Recombination Rates of H_2 and O_2 over Pure and Impure Plutonium Oxides** Luis Morales NMT Division
- ❖ **Radiochemical Experiments of Water Adsorbed Onto Actinide Oxides** Lav Tandon NMT Division
- ❖ **Model Studies of Interfacial Reactions Of Water Adsorbed On Actinide Oxides** Mark Paffett CST Division
- ❖ **Model for Gas Evolution in PuO_2 Containers** John L. Lyman CST Division



Deliverables

- 1) Peer reviewed publication(s) submitted on surface science investigations of Small Molecule-U/ UO_2 interactions.
- 2) Peer reviewed publication submitted on H_2/O_2 recombination rates over PuO_2 and other MeO_2 samples with fluorite structures
- 3) LAUR report submitted on initial surface science investigations of H_2O -Pu/ PuO_2 interactions.
- 4) Peer reviewed publication submitted on Small Molecule(H_2O)-Pu/ PuO_2 interactions.
- 5) Peer reviewed publication on interaction of H atoms with UO_2 surfaces
- 6) Quarterly reports as requested
- 7) Project personnel also will be available for technical discussions, periodic program reviews and response as appropriate to unforeseen 94-1 issues as they arise.

Major Achievements and Deliverables

Uranium Work

Disassociative bond breaking chemistry of adsorbed water by radiolytic processes

Characterization of UO_x defect sites using novel adsorbed chemical probes.

UPS valence band studies of oxide versus hydroxyl surface species.

Understand role of hydroxide produced using radiolytic modeling experiments (H atom doser)

Adsorption and thermal decomposition of adsorbed water for defected UO_2 surfaces

Major Achievements and Deliverables

Uranium Work (Continued)

Interaction of adsorbed water species with adventitious hydrocarbons
(e.g., $\text{H}_2\text{O}_{\text{ads}} + \text{CO}_{2\text{ads}} \rightarrow \text{HCOO}_{\text{ads}}$)

Infrared reflection adsorption spectroscopy experiments on planar substrates (UO_2).

Infrared transmission studies of pressed high purity powders of the oxides of uranium initiated using existing instrumentation

Production and reactivity of higher oxides of U using oxidants such as NO_2 .



Major Achievements and Deliverables

Plutonium Work

TGA, PVT, and XRD applied to the study of $\text{H}_2 + \text{PuO}_x \rightarrow \text{PuO}_{x-y} + \text{H}_2\text{O}$

TGA, PVT, and XRD applied to the decomposition and gas analysis of PuO_{2+x} .

Kinetics of hydrogen production as a function of water vapor pressure over pure and impure PuO_2

Isosteric heat of adsorption measurement of reaction:

$\text{PuO}_2 + x\text{H}_2\text{O} \rightarrow \text{PuO}_2(x\text{H}_2\text{O})$ Expts will yield true equilibrium constant values for water reactivity at relevant partial pressures

Continue PVT investigation of H_2/O_2 recombination rates at different H_2/O_2 ratios and temperature

Major Achievements and Deliverables

Plutonium Work (Continued)

Survey other small molecule systems that might possibly lead to deleterious gas generation

Oxidation surface chemistry of Pu metal to make “well characterized” reproducible planar Pu oxide surfaces for future water sorption studies (XPS and Auger spectroscopy)

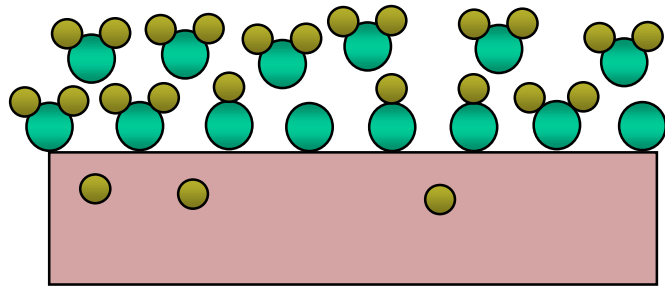
Characterize Pu oxide powder starting materials (clean Pu oxide particulate or pressed pellet) (XPS spectroscopy)

Water reactions at Pu oxide powder (particulate or pressed pellet) (XPS spectroscopy)

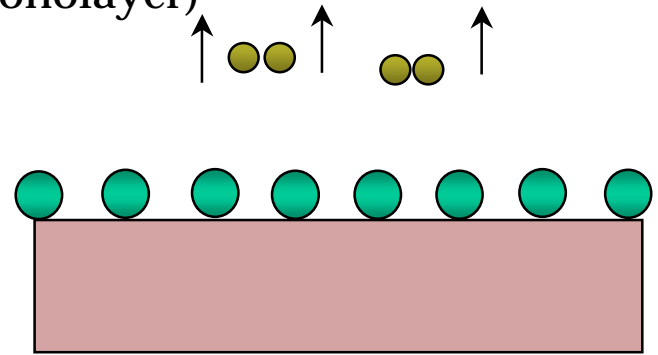


Thermodynamics of D₂O Chemistry on Metal Oxides (Including Actinides)

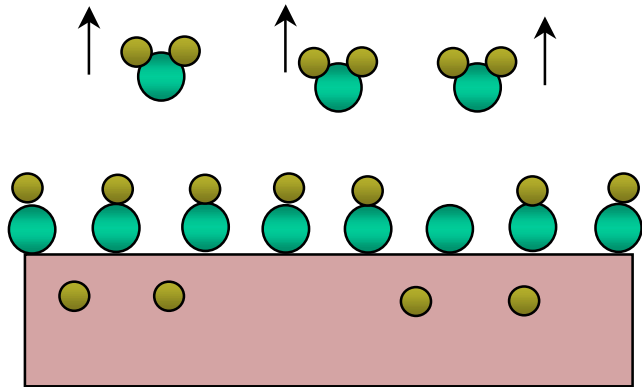
Initial Coverage (> 1 monolayer)



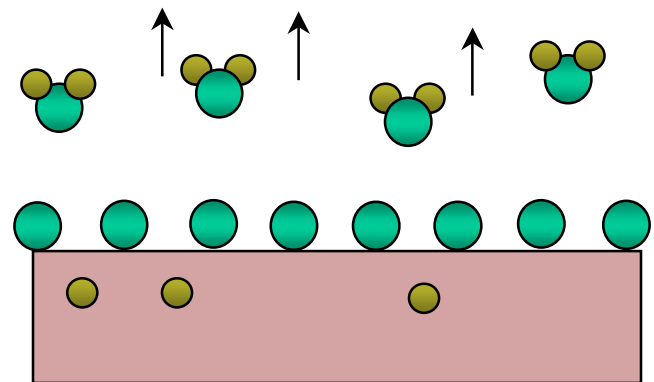
desorption of D₂O from oxide 10-12 kcal m⁻¹
desorption of D₂O from hydroxyls 15-25 kcal m⁻¹



recombination of deuterium atoms
leading to H₂ desorption;
for UO₂ ~38 kcal m⁻¹



Associative recombination of surface hydroxyls
PuO₂ 41 kcal m⁻¹



Representative Values For Water Desorption Processes From Metal Oxide Surfaces

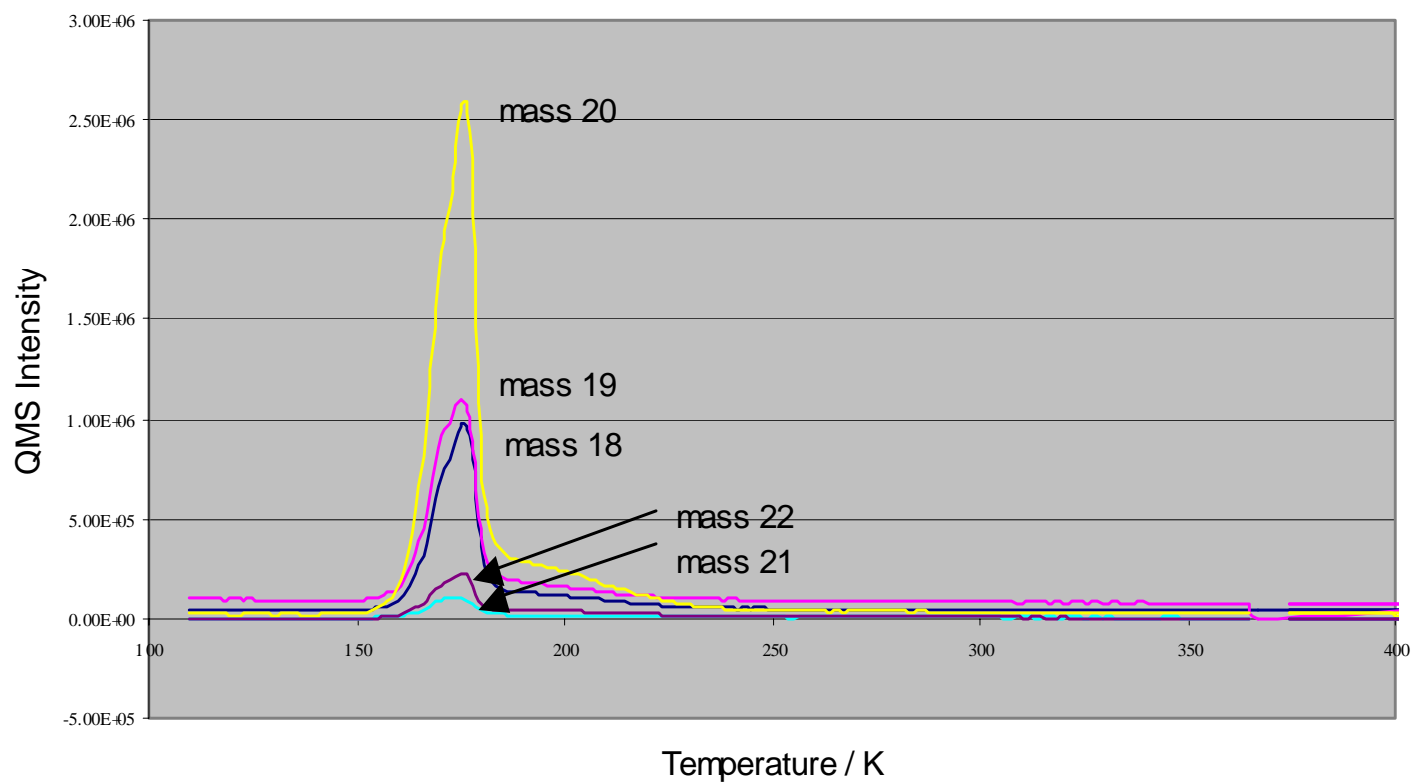
Reversible Adsorption from Metal Oxide Surface

M_xO_y	DH_{des} (kJ m ⁻¹)	Ref
a-Fe ₂ O ₃ (012)	41.8	Henderson et al, SS, 1998
a-Fe ₂ O ₃ (001)	42	Hendewerk, et al, SS, 1986
a-Fe ₂ O ₃ -poly xtal	42.6 (multilayer) 61.44 (monolayer)	Murray, et al , JVST, 1995
Cr ₂ O ₃	-----	Morishige et al, JPC, 1981
NiO	44	Kuch et al, FJAC, 1995
UO ₂	44.3	Manner et al , JNM, 1999
PuO₂	83.6	Stakebake, JPC, 1973

Associative Recombination of Surface Hydroxyls

M_xO_y	DH_{des} (kJ m ⁻¹)	Ref
a-Fe ₂ O ₃ (012)	120	Henderson et al, SS, 1998
a-Fe ₂ O ₃ (001)	54-195	Hendewerk, et al, SS, 1986
a-Fe ₂ O ₃ -poly xtal	-----	Murray, et al , JVST, 1995
Cr ₂ O ₃	~170	Morishige et al, JPC, 1981
NiO	~150	Kuch et al, FJAC, 1995
UO ₂	-----	Manner et al , JNM, 1999
PuO₂	284.2 (?)	Stakebake, JPC, 1973

Thermal Desorption of $D_2^{16}O$ from $U^{18}O_2$ Interface: Facile Exchange of Oxygen Isotopes



Reaction rates for $\text{H}_2 + \text{O}_2$ over PuO_2 and vacuum treated PuO_2

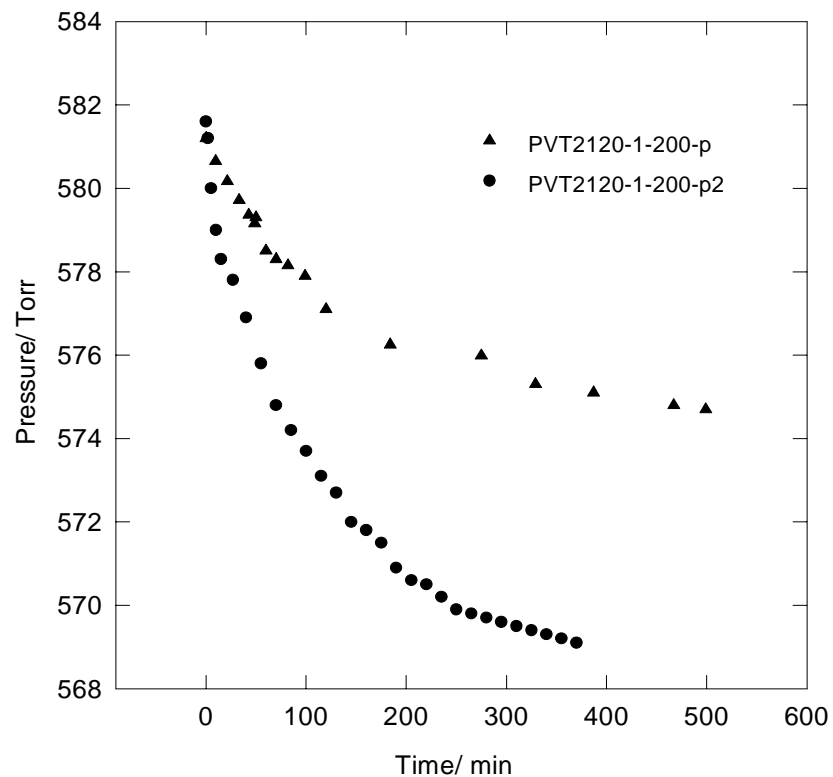
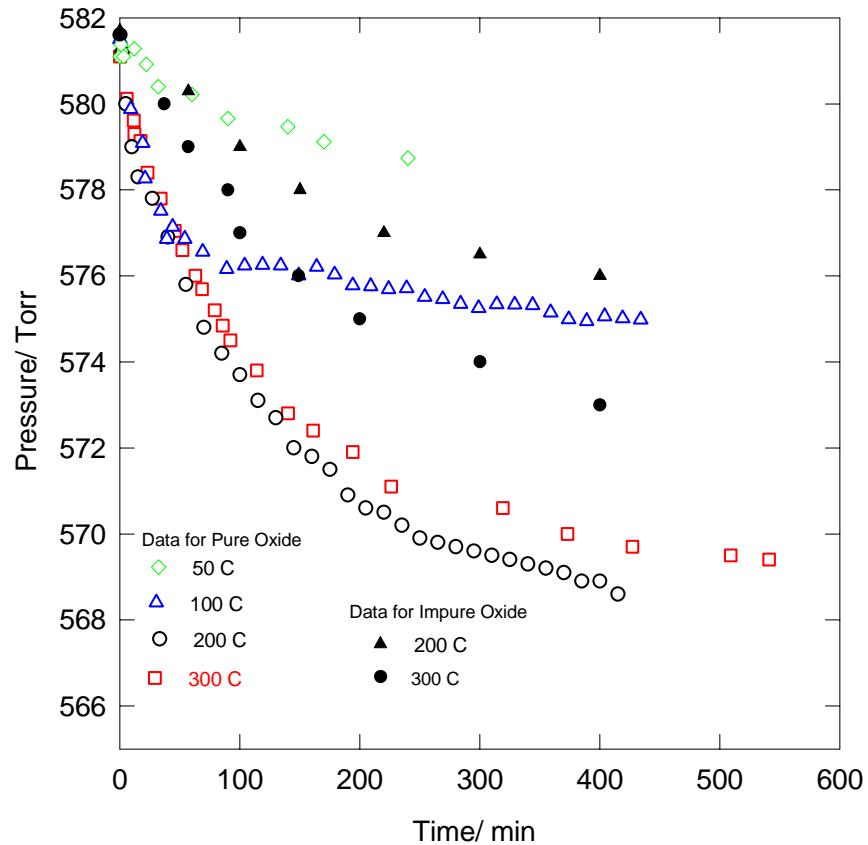


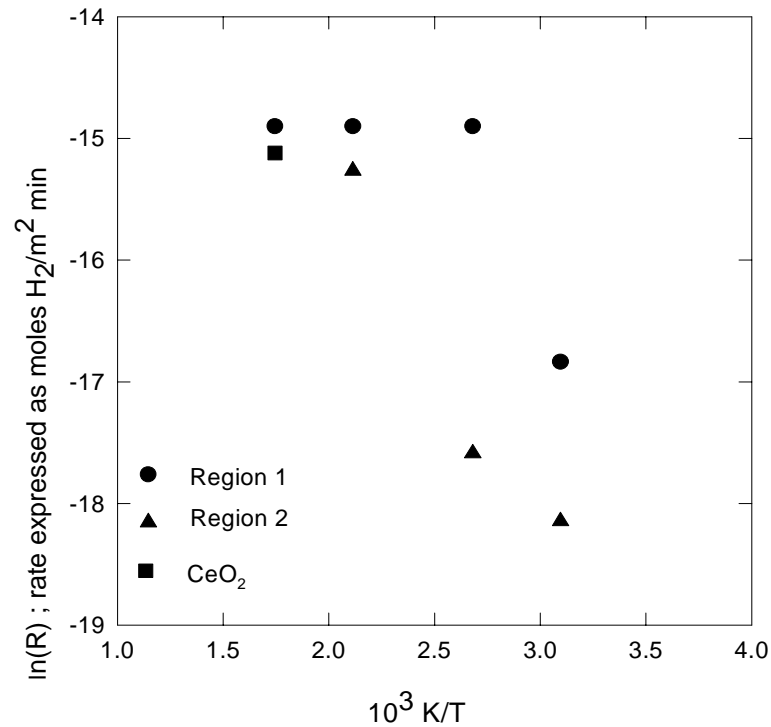
Figure 3. Pressure-time curves obtained at 200 °C for the pure oxide showing the effects that heating under dynamic vacuum have on the reaction rate. In experiment PVT2120-1-200-p the sample was not pre-treated.

Reaction rates for $\text{H}_2 + \text{O}_2$ over PuO_2 and impure PuO_2 versus reaction temperature



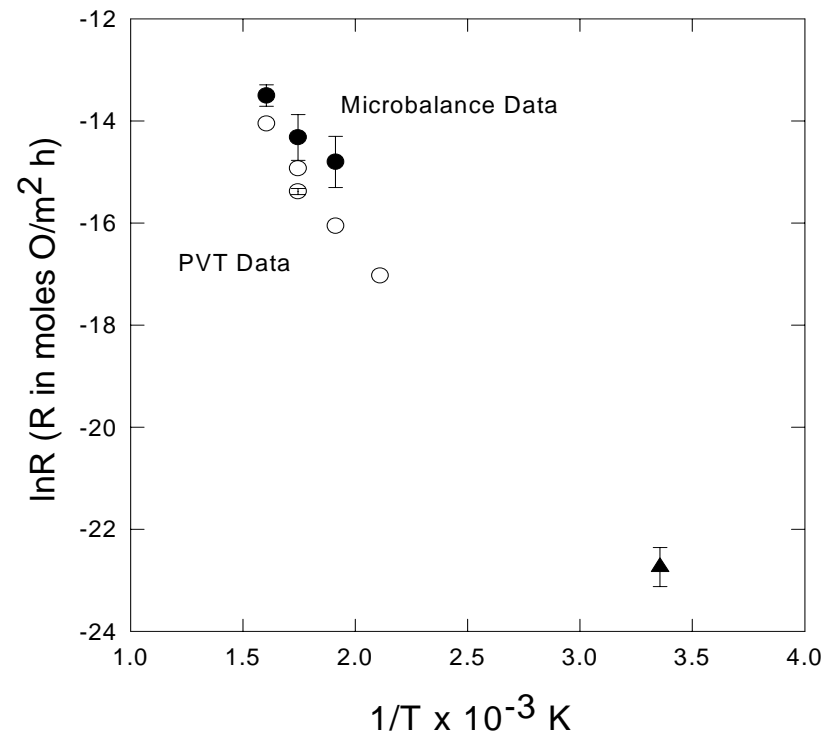
Survey Reactions ($\text{H}_2 + \text{O}_2$ and H_2O Reaction) Over PuO_2 and Fluorite Metal Oxides

Reaction rates for
 $\text{H}_2 + \text{O}_2$
over PuO_2 and CeO_2



Reaction rates for
 H_2O vapor
over PuO_2

Arrhenius Data for $\text{PuO}_2/\text{H}_2\text{O}$ Reaction



Surface Chemical Reactions: Conclusions

👍 Work on radioactive actinide materials shows that the recombination is surface catalyzed.

- Role of active sites demonstrated
- CeO_2 is effective
- Resolve different kinetic regions each with large temp. dependence
- Water acts as an inhibitor during the recombination reaction

👍 Steady-state is reached

- Rates of recombination and water radiolysis equalized

👍 Demonstrated that H_2 generation is $[\text{H}_2\text{O}]$ dependent



Radiochemistry Studies: Microdosimetry

- **Modeling Studies**

- Theoretical model calculations are being used to predict the range, the energy distribution, and the radiation damage due to alpha particles using advanced computer simulations based on Monte Carlo methods and the Stopping and Range of Ions in Matter (SRIM)-2000.39 program.

- **Experimental Studies**

- Experiments are being designed to measure the total dose coming out of actual different size PuO_2 particles.
- Chemical dosimetry and Counting techniques



Radiation Chemistry

- **Experimental Studies**

- Hydrogen production will be determined from absorbed water on the plutonium surrogates: CeO_2 , Pr_2O_3 , UO_2 , $^{244}\text{PuO}_2$ or $^{242}\text{PuO}_2$ etc., irradiated with 5 - 0 MeV alpha-particles. Experiments will focus on the following:

- Water % loading
 - Particle size
 - Surrogate effects
 - Impurity effects (salts, sulfates, and nitrates)
 - Estimation of bulk water product yields



Gas Generation Modeling

Why?

- 👍 Radiolysis and chemical processes in storage and transport of plutonium oxides may generate gases
- 👍 Internal pressure may damage containers
- 👍 Gas may be flammable (H_2)
- 👍 Model can guide experiments and predict gas generation

Container standard restricts contents and processing

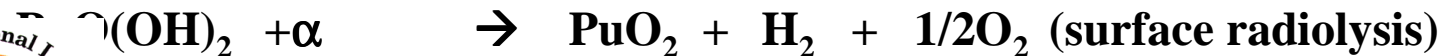
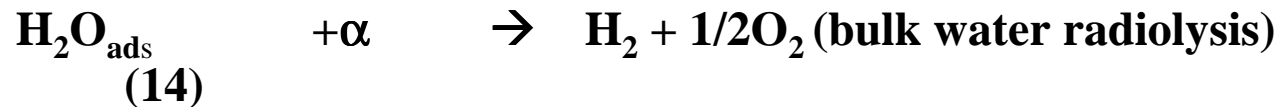
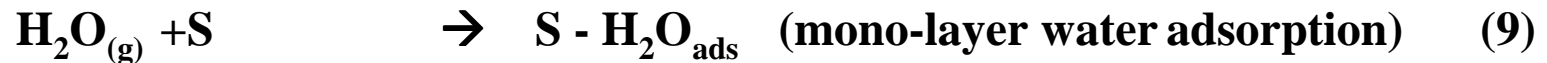
- 👍 <5 kg material
- 👍 > 30% plutonium
- 👍 <19 W heat generation
- 👍 <700 psi internal pressure
- 👍 >2 hours calcination at 950°C
- 👍 <0.5% H₂O (25 g)

Model for Gas Evolution in PuO₂ Containers

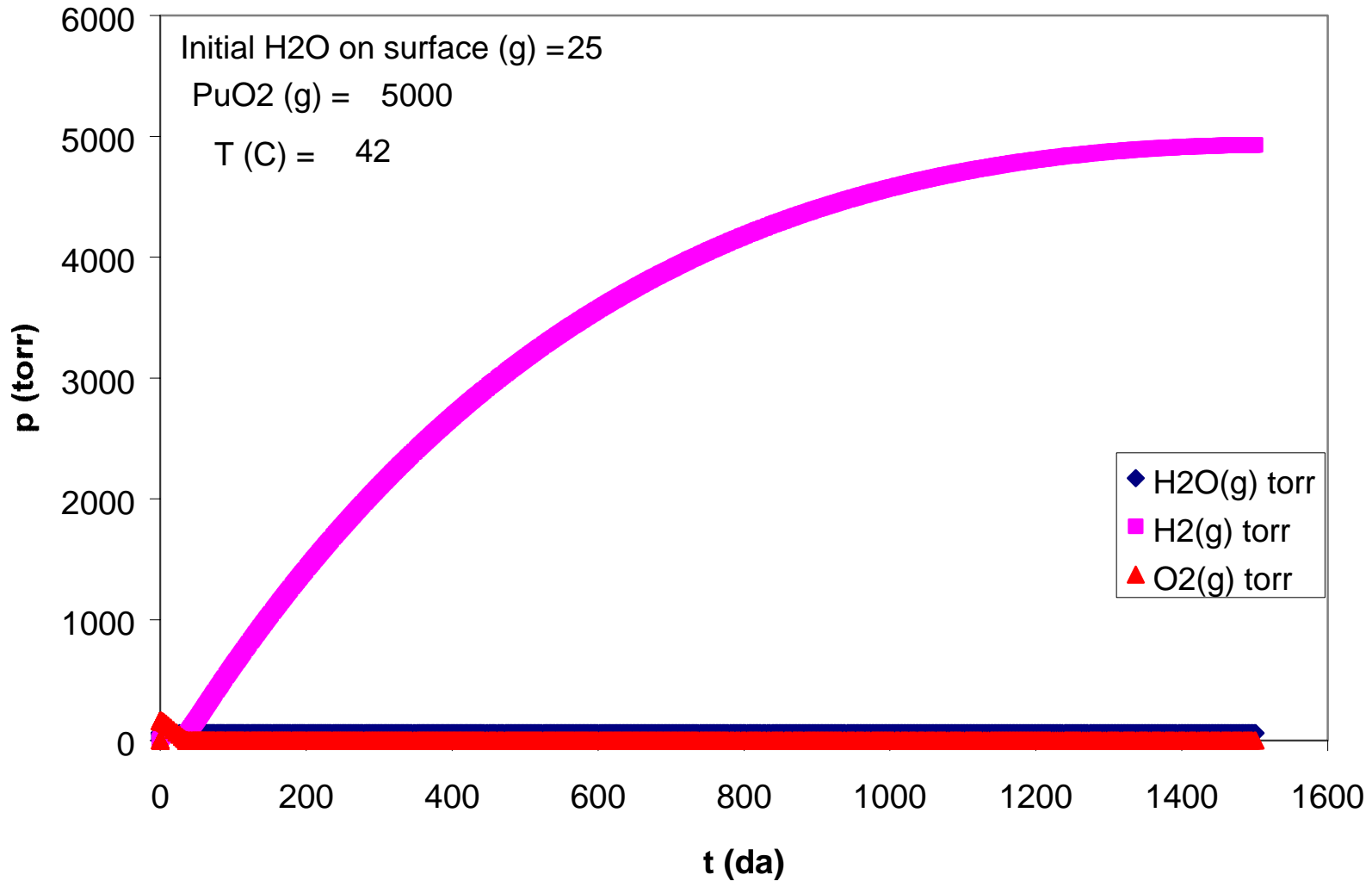
- 👍 Reflects physical characteristics of the 3013 transport container
- 👍 Includes properties of contents (alpha flux, measured surface area, etc)
- 👍 Solves rate equations to give gaseous, surface, condensed species
- 👍 Uses measured, preferably published, rates of fundamental processes
 - surface adsorption and evaporation of water
 - Alpha radiolysis of adsorbed water to H₂ and H₂O₂
 - Radiolytic recombination of H₂ and O₂ to water
 - Catalytic recombination of H₂ and O₂ to water
 - Oxidation of PuO₂ to PuO_{2+x} by O₂ and H₂O₂
 - Published or estimated thermochemical parameters
- 👍 Written in Visual Basic for Excel and is simple to run with a PC
- 👍 Improvements and expansion to other materials in progress

Reaction Set Used in Kinetic Modeling of Gas Generation

(All reactions are first order)



Gases



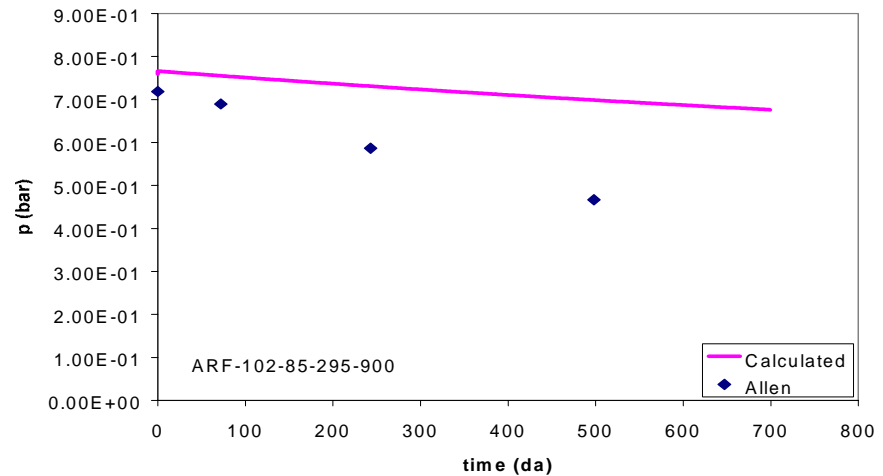
Gas Generation Modeling: Test Case

Pressure

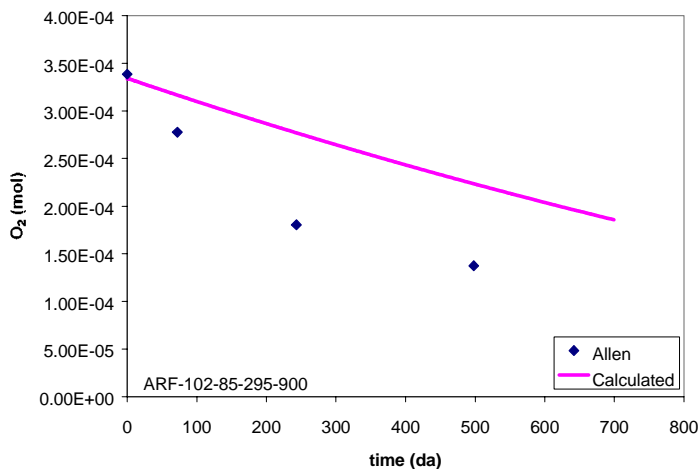
Sample AFL-102-85-900

Initial Conditions

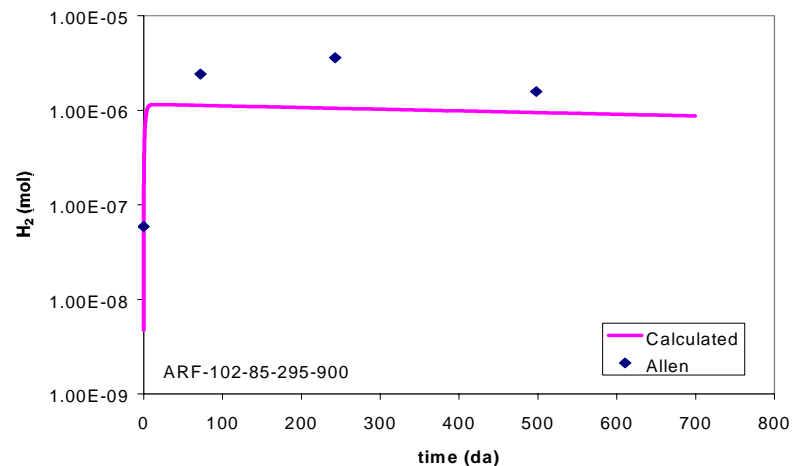
Volume (ml)	70
PuO ₂ (g) =	10
H ₂ O present (μg)	70
N ₂ (torr)	466
O ₂ (g) (torr)	124
p(bar)	0.79
Surface area (m ²)	50
Total H ₂ O monolayers	1.86



Oxygen

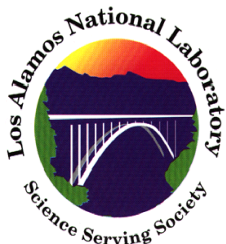


Hydrogen



Conclusions From Combined Modeling Effort

- 👍 Calcining prevents most gas generation
- 👍 Adsorbed water may produce hydrogen
- 👍 Model suggests:
 - O_2 consumed before H_2 levels rise
 - H_2 levels may rise after O_2 reacts
 - Experiments to characterize PuO_{2+x}
 - What radiolysis products arise from physically and chemically adsorbed water?
 - What are G values for adsorbed water and how to incorporate them into model?



Acknowledgements

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NMT Division

94-1 Core Technology Program